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6. AUTHOR(S)

J. G. Verkade

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Iowa State University
Department of Chemistry
Ames, IA 50011

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13. ABSTRACT (Maximum 200 words)

An exploration of the chemistry of silatranes and azasilatranes has been carried out. The first isolation and structural characterization of silatrane adducts in which the exocyclic axial oxygen behaves as a Lewis base site was accomplished. Azasilatrane phosphine-nitrogen complexes were prepared with Lewis acid sites on the complex bonding to the axial oxygen. An axial silatranium cation was prepared. The range of axial-substituents for azasilatranes was explored and found to be limited to H, OR, OAr, R, and Ar. Attempts to obtain pentacoordination by nitrogen by replacing the axial hydrogen by azide using trimethylsilylazide resulted instead in trimethylsilyl substitution of the equatorial nitrogens and an azide salt. Pyrolysis of the azide salt afforded the pentacoordinated azide. Nitrogen pentacoordination was also obtained from a thioisocyanide salt. A number of other equatorial nitrogen substituted azasilatranes were prepared. Attempts to couple azasilatrane to a Si-Si bonded dimer were unsuccessful. Azasilatrane-based polymers were prepared and characterized. The azasilatrane studies were extended to azastannatranes.

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Final Technical Report

J. G. Verkade

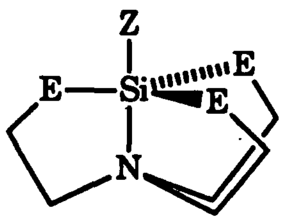
AFOSR-88-0081

November 1, 1987 - October 30, 1990

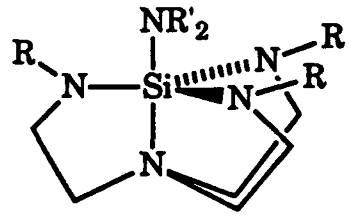
It should be noted at the outset that the PI's research described in this section was supported by one three-year AFOSR grant which expired October 31, 1990. A preproposal for renewal was approved by the AFOSR June 12, 1990 and the full proposal based on the preproposal was mailed July 20, 1990. On July 30 the PI was informed by telephone by the AFOSR that although this new departure in our research program had been unusually productive, recent fiscal cutbacks and changes in programmatic priorities necessitated that the full proposal be declined without review.

The primary objectives of the AFOSR grant were:

A. Exploration of the chemistry of silatranes such as 1 and azasilatranes such as 2.



**1** Z = R, OR; E = O
**2** Z = R, OR; E = NR



**3**

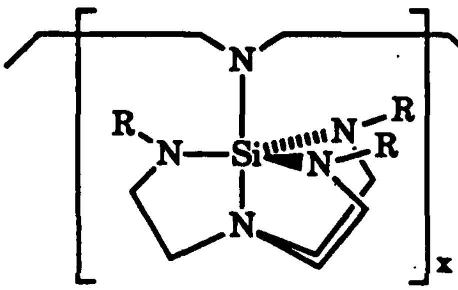
B. Synthesis of silatranes in which silicon is pentacoordinated by nitrogens as in 3.

C. Synthesis of oligomers/polymers containing azasilatrane repeating units.

All three of these objectives were achieved.

Though beyond the scope of the AFOSR grant, the eventual goal towards which our research was directed was the synthesis of polymers such as 4 and 5 which might serve as precursors to essentially pure silicon nitride, with minimum contamination by silicon carbide, owing to the robustness of the chelated hypercoordinated silicon and the presence of only Si-N bonds in the azasilatrane cage.

What follows is a summary of the work associated with the objectives A-C given above.



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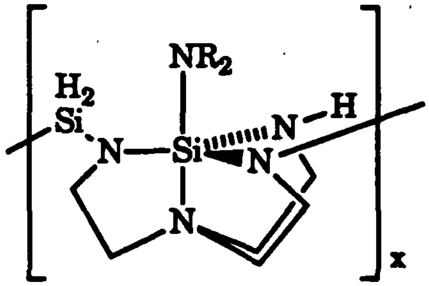


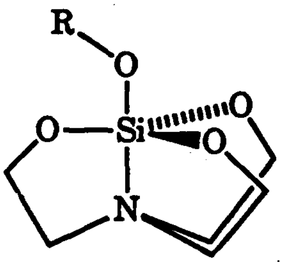
5

**A. Exploration of the chemistry of silatranes and azasilatranes**

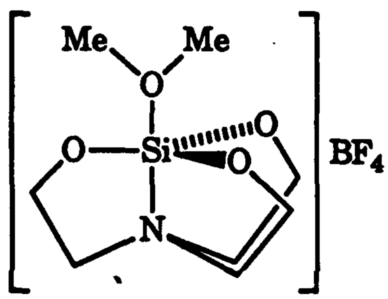
In order to construct polymers of types **4** and **5**, it was necessary to gain some knowledge of the reactivities (nucleophilicities) of the exocyclic axial, the equatorial, and the endocyclic axial substituents on the silicon in **1** and **2**. The chemistries of these reactivity sites are now addressed in turn.

**1. Reactivity of the axial substituent in silatranes and azasilatranes**

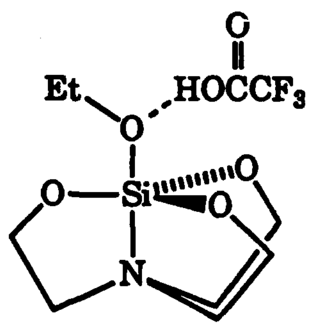
The equatorial and axial oxygens in alkoxy silatranes such as **6** and **7** might be



| | R |
|---|---|
| **6** | Me |
| **7** | Et |



**8**($BF_4$)



**9**

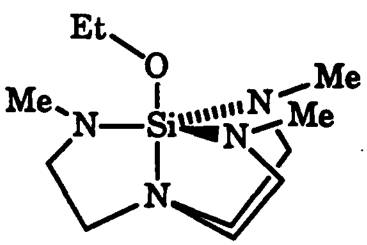
expected to display increased basicity owing to electron induction into silicon by the *trans* axial tertiary amino nitrogen. We recently reported the first isolation and structural characterization of silatrane adducts in which the exocyclic axial oxygen behaves as the Lewis basic site.[1] Thus silatranes **6** and **7** are fully covalently bonded and hydrogen bonded to their Lewis acid components in the structures of **8**($BF_4$) and **9**, respectively. The $SiN_{ax}$ bond length decreases considerably (~0.5 Å) from **7** to **8**($BF_4$) (1.965(5) Å) and the

latter is the shortest such bond distance reported for any silatrane. The O(H)O distance in **9** (2.489 Å) is the shortest reported for an unsymmetrical hydrogen bond. The $SiO_{ax}$ distance increases by a total of 0.17 Å in the order **7** < **9** < **8**($BF_4$).

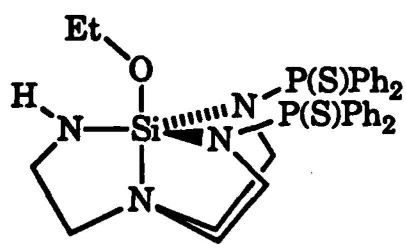
Interestingly, cation **8** is the first reported example of a silatrane having an ideal TBP symmetry. Thus all others that have been structured contain silicon atoms that are at least ~0.1 Å above the $O_{eq}$ plane. In this connection we have shown[1] that a prediction[2] that an ideally TBP silatrane should possess an Si-$N_{ax}$ distance of 1.83 Å is incorrect by more than 0.1 Å.

Measurement of phenol ν(OH) shifts reveals the basicity order $(Me_3Si)_2O$ < $Si(OR)_4$ < alkoxy silatranes ≤ $Me_3SiOMe$ < $Et_2O$. While this trend places the electron inductive ability of the silatranyl group ahead of $(RO)_3Si$, it is below that of an Et group.

Until we began the work supported by the AFOSR grant, there were only four azasilatranes (**2**) reported and very little was known about them. Structural evidence is accumulating, however, that these compounds possess Si-$N_{ax}$ bonds at least as robust as those in silatranes (**1**).[3,4] This is somewhat unexpected in view of the greater electronegativity of the equatorial oxygen substituents in **1** than in **2**. Thus the Si-$N_{ax}$ bond lengths in **10**,[3] **11**[4] and **12**[4] are very comparable to that in **7**.[1] That the ethoxy oxygen



**10**



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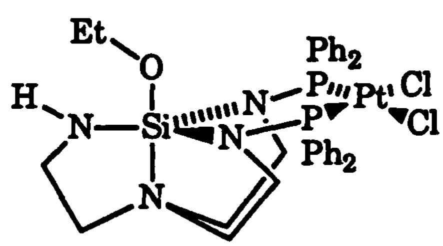
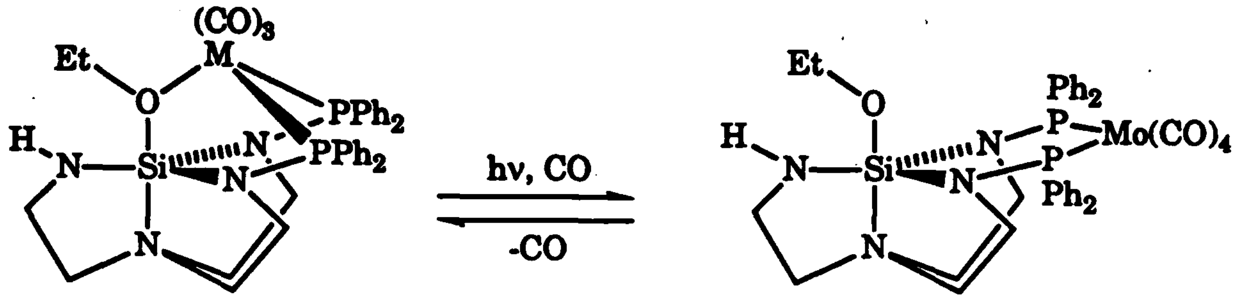


**12**

in these azasilatranes also displays Lewis base character is evident in complexes **13** and **14** which can be converted to **15** and **16**, respectively in the presence of CO.

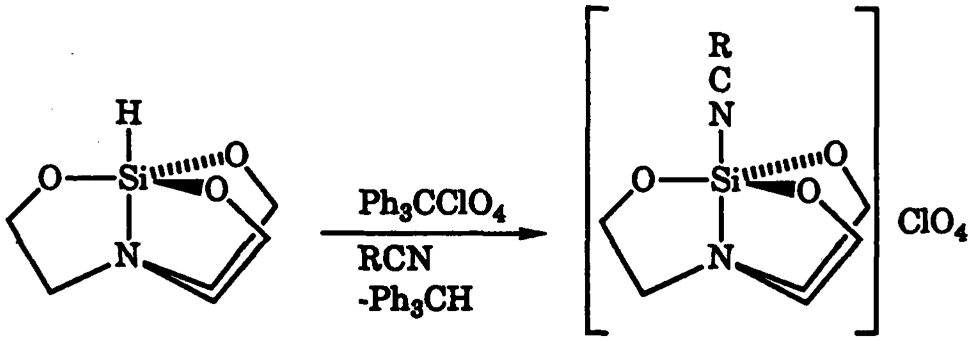


(1)

13 M = Mo 15

14 M = W 16

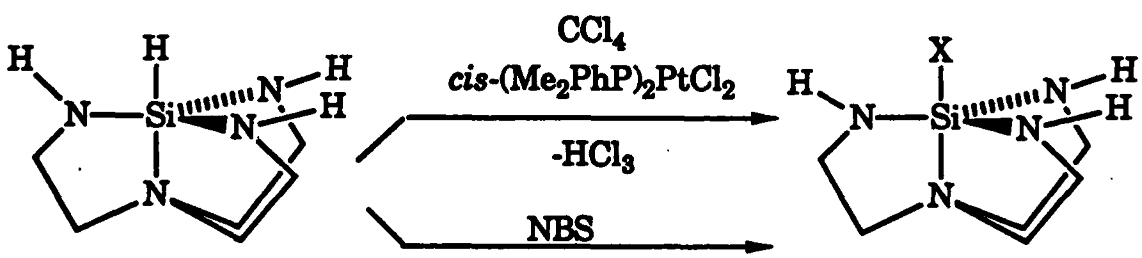
We carried out several interesting substitution reactions at the axial position. In reaction 2 the synthesis of the novel silatranium cation **18** is realized under very mild



(2)

17 18

conditions.[5] Compound **18** is, however, very resistant to nucleophilic attack by $F^-$, $H^-$ and $^-OR$.



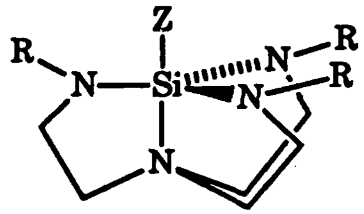
20 X Cl (3)

21 Br (4)

19

We converted azasilatrane **19** to **20**[3] and **21**,[6] which we planned to use as precursors to amido azasilatranes. Unlike silanes,[7] **19** is unreactive to Si-H proton substitution by

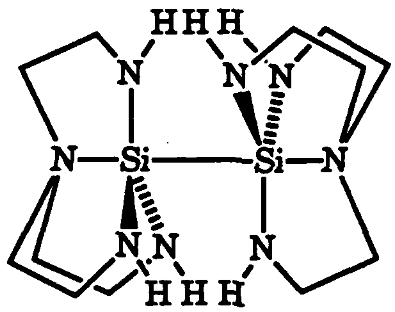
amide.[3] Unfortunately the range of Z groups in **22** formed via reaction 5 seems to be restricted to Z = H, OR, OAr, R and Ar.[3]

$N(CH_2CH_2NHR)_3 + ZSi(NMe_2)_3 \longrightarrow$  (5)



**22**

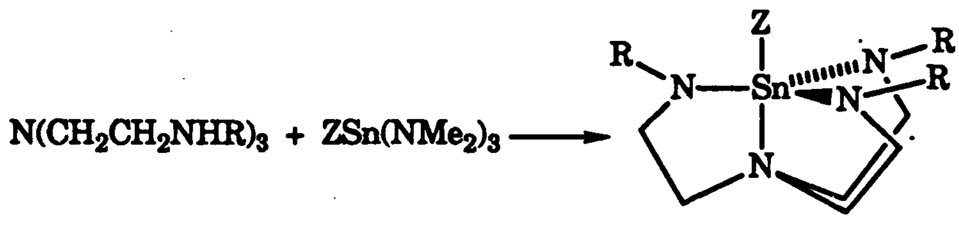
Attempts to synthesize the novel structure **23**, which because of its zero dipole dipole moment, may be a volatile MOCVD precursor for SiN, were unsuccessful.[8]

**20** $\xrightarrow{Na(Hg)}$  (6)



**23**

The above studies were being extended to azastannatranes such as **24-27**, a class of compounds we synthesized for the first time.[6] A most curious observation in the crystal structure determination of azastannatrane **26** is that the two independent molecules in the unit cell possess substantially different Sn-$N_{ax}$ bond lengths of 2.380(2) and 2.453(2) Å.[9] Two different $^{119}Sn$ chemical shifts in the solid state have also been observed.[9] The most reasonable rationale for this observation is differences in crystal packing forces. This rationale has also been advanced[10] to account for the observation that silatranes in the solid state, such as those we have structured, frequently exhibit shorter Si-$N_{ax}$ distances than are found calculationally or in the gas phase by electron diffraction.



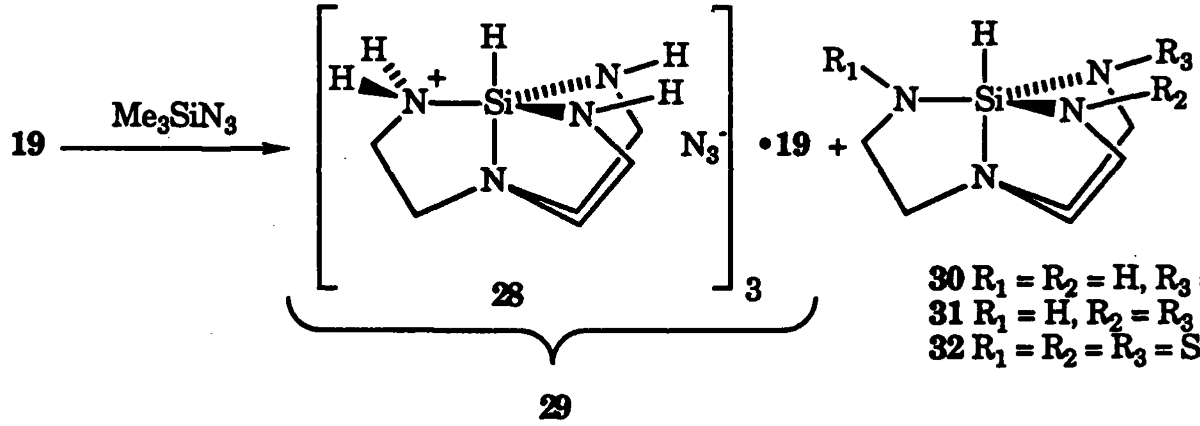
| | Z | R |
|---|---|---|
| **24** | *n*-Bu | Me |
| **25** | Ph | Me |
| **26** | Ph | H |
| **27** | $NMe_2$ | Me |

(7)

### 2. Reactivity of the equatorial substituent in silatranes and azasilatranes

Discussed in this section are addition of $H^+$ and $R^+$ to an $N_{eq}$ site, displacement of the $N_{eq}$-H hydrogen by R, and solvolytic cleavage of Si-$N_{eq}$ bonds.

In a recent communication[11] we reported the synthesis of **28** , the first stable representative of incipient proton-assisted equatorial bond cleavage of a five-coordinate intermediate to be isolated.[11] Reaction 8 actually constituted an attempt to substitute the



**28**

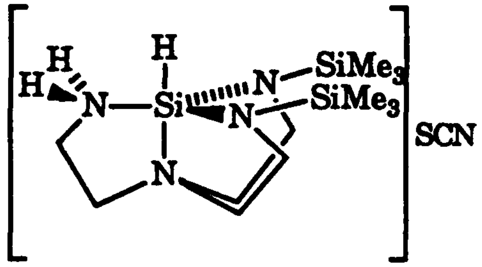
**29**

**30** $R_1 = R_2 = H, R_3 = SiMe_3$
**31** $R_1 = H, R_2 = R_3 = SiMe_3$
**32** $R_1 = R_2 = R_3 = SiMe_3$

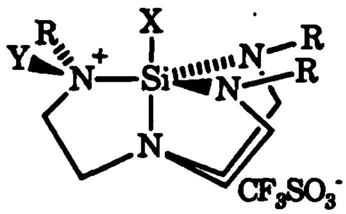
(8)

axial proton of **19** by azide. Instead, $Me_3Si^+$ attacks $N_{eq}$ sites, liberating the protonating agent $HN_3$. Interestingly compound **28** co-crystallized with **19** in the unit cell of **29**. The molecular structure of **29**[11] as well as its analogue **33**,[12] determined by X-ray means, revealed that in each case the Si-$\overset{+}{N}_{eq}H_2$ length is ca. 10% longer than the two Si-$N_{eq}$H bonds in this cation. By analogous reactions of azasilatranes with MeOTf and $Me_3SiOTf$, the new salts **34-39** were synthesized.[13]

We carried out a variety of substitution reactions at the $N_{eq}$-H function in azasilatranes as exemplified by reaction 9 and Scheme I.[3,14] Though the sterically elongated Si-$N_{ax}$ distance in **51** (2.775(7) Å) is the longest ever recorded in an azasilatrane,

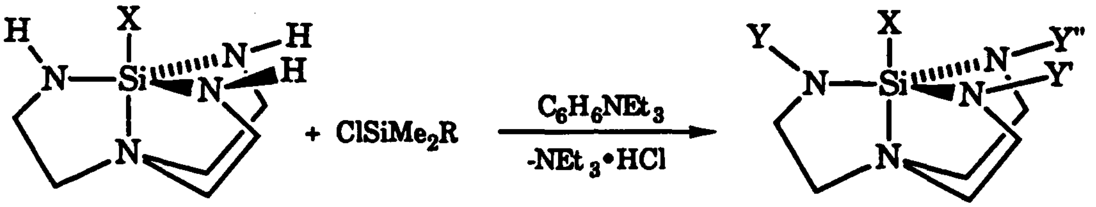


33



| | X | R | Y |
|---|---|---|---|
| 34 | H | Me | Me |
| 35 | H | Me | $SiMe_3$ |
| 36 | H | $SiMe_3$ | Me |
| 37 | Me | Me | Me |
| 38 | Me | Me | $SiMe_3$ |
| 39 | Me | $SiMe_3$ | $SiMe_3$ |

it is 24% shorter than the sum of the van der Waals radii, suggesting some degree of silicon interaction with the nearly planar $N_{ax}$.[14]



(9)

| | X | R | | X | Y | Y' | Y" |
|---|---|---|---|---|---|---|---|
| 19 | H | Me | 41 | H | $SiMe_3$ | $SiMe_3$ | $SiMe_3$ |
| 19 | H | H | 42 | H | $SiMe_2H$ | $SiMe_2H$ | $SiMe_2H$ |
| 19 | H | Ph | 43 | H | $SiMe_2Ph$ | $SiMe_2Ph$ | $SiMe_2Ph$ |
| 19 | H | *t*-Bu | no reaction | | | | |
| 40 | OEt | H | 44 | OEt | $SiMe_2H$ | $SiMe_2H$ | $SiMe_2H$ |
| 40 | OEt | Me | 45 | OEt | $SiMe_3$ | $SiMe_3$(H) | H |
| 40 | OEt | Ph | 46 | OEt | $SiMe_2Ph$ | $SiMe_2Ph$(H) | H |
| 40 | OEt | *t*-Bu | no reaction | | | | |

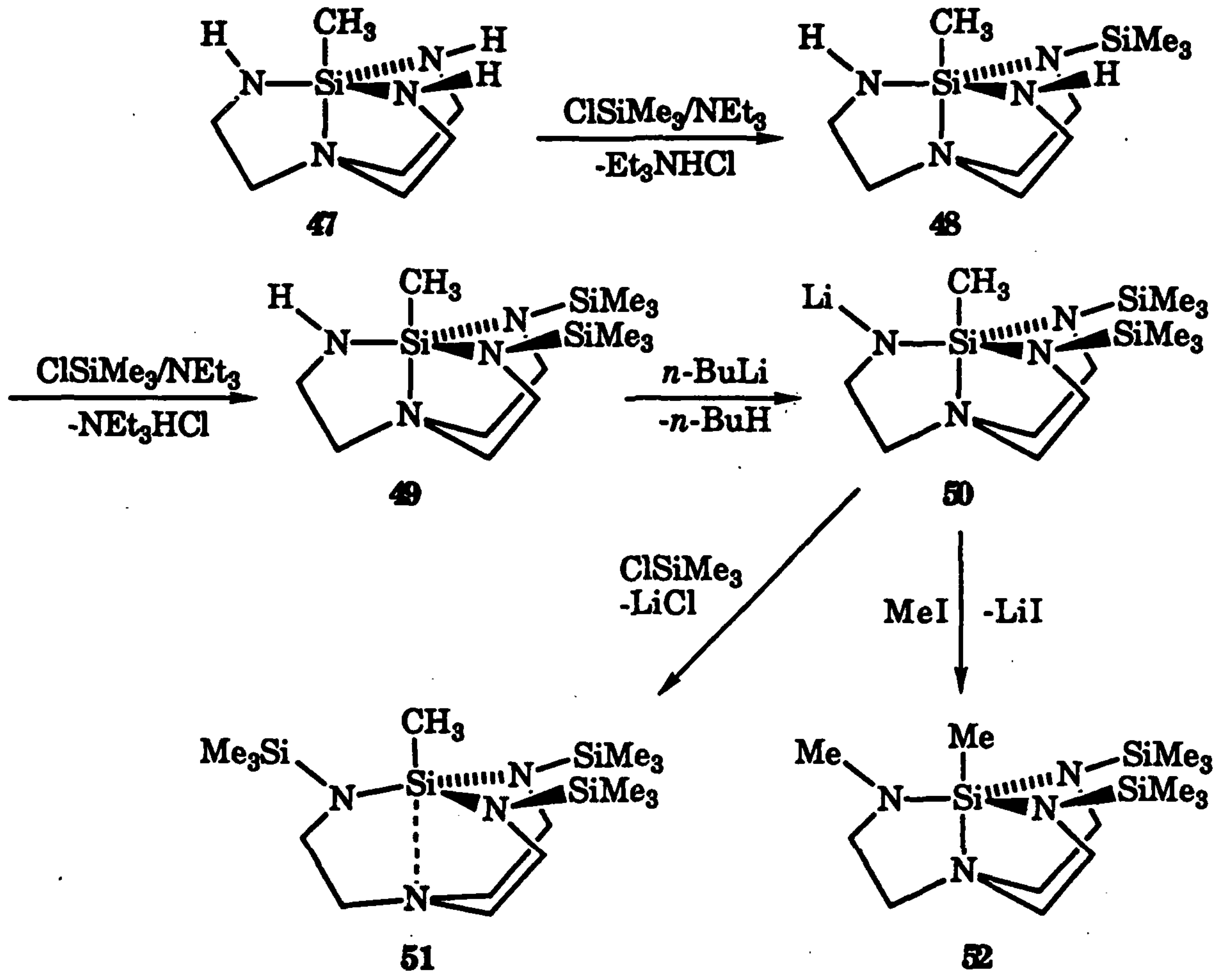
Solvolysis experiments on azasilatranes with MeOH revealed that the Si-$N_{eq}$ bond is more sensitive than the axial Si-H, Si-OEt or Si-$CH_3$ bond.[15] In Schemes II-V it is seen that a) solvolysis of the substituent on $N_{eq}$ may or may not precede Si-$N_{eq}$ bond cleavage and b) monocyclic solvolysis intermediates are sometimes detected.

The rate and pathway of methanolysis appear to be strongly dependent on the strength of the $N_{eq}$-substituent bond and on the steric crowding these groups experience with the exocyclic axial group.[15]

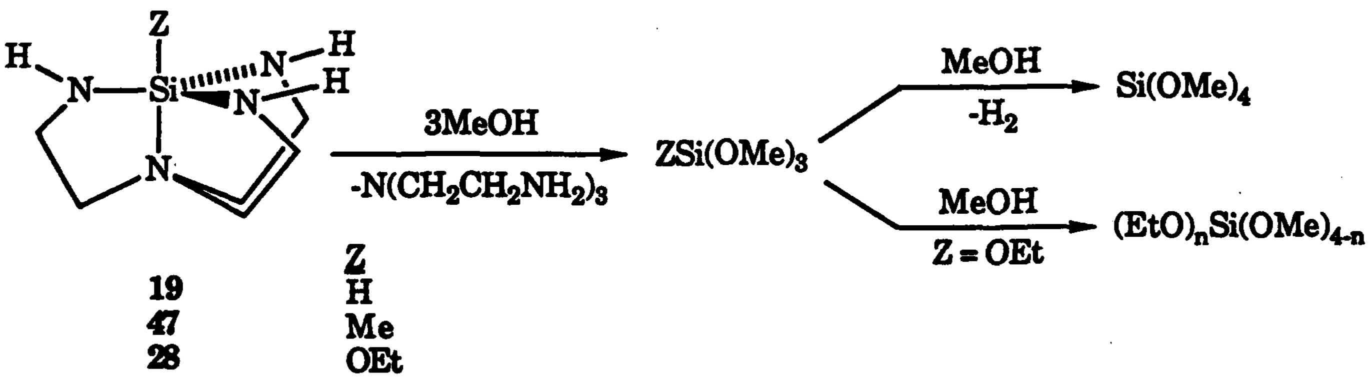
### 3. Reactivity of the endocyclic axial substituent in azasilatranes

Although substantial Si-$N_{ax}$ bond strength in azasilatranes is afforded by the presence of the three chelating five-membered rings, weakening of this bond has been seen to occur in the previous section by steric crowding (e.g., 51) and cleavage can take

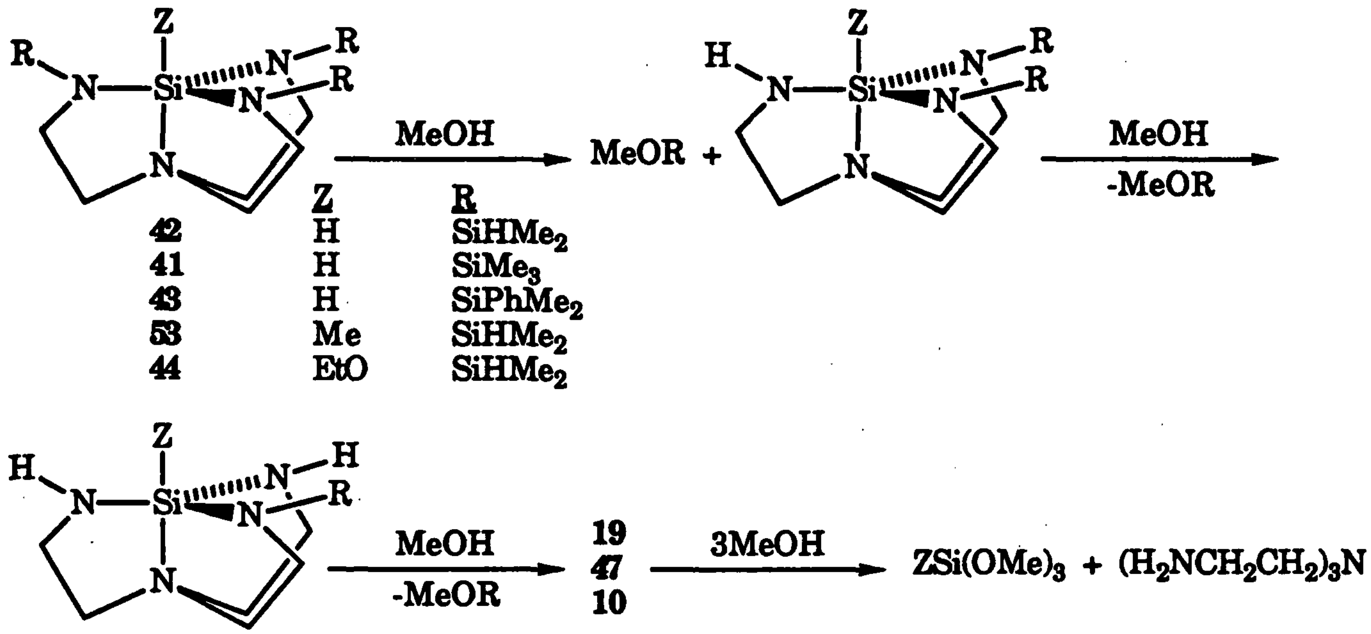
**Scheme I**



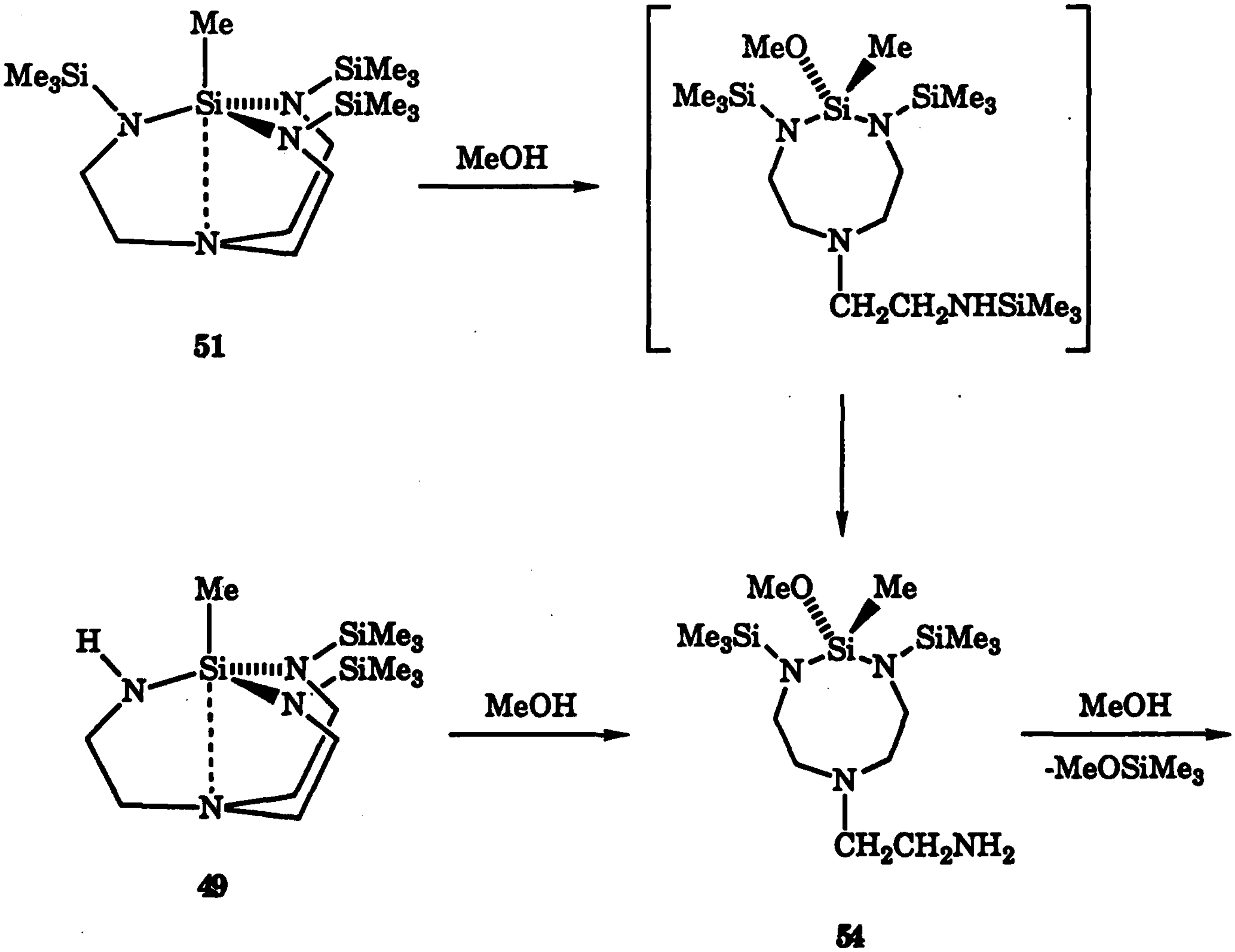

**Scheme II**

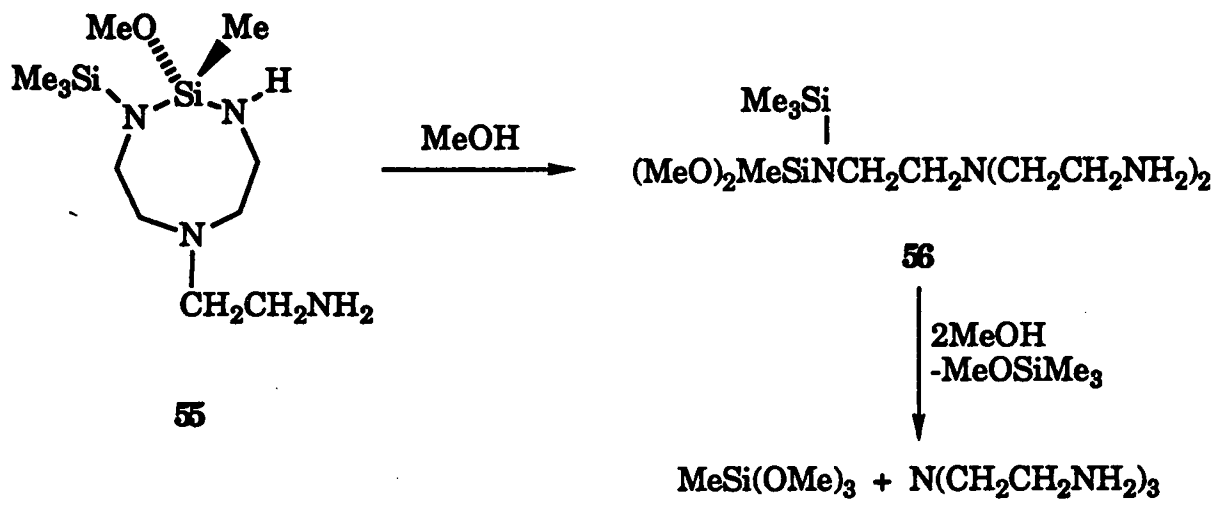


**Scheme III**



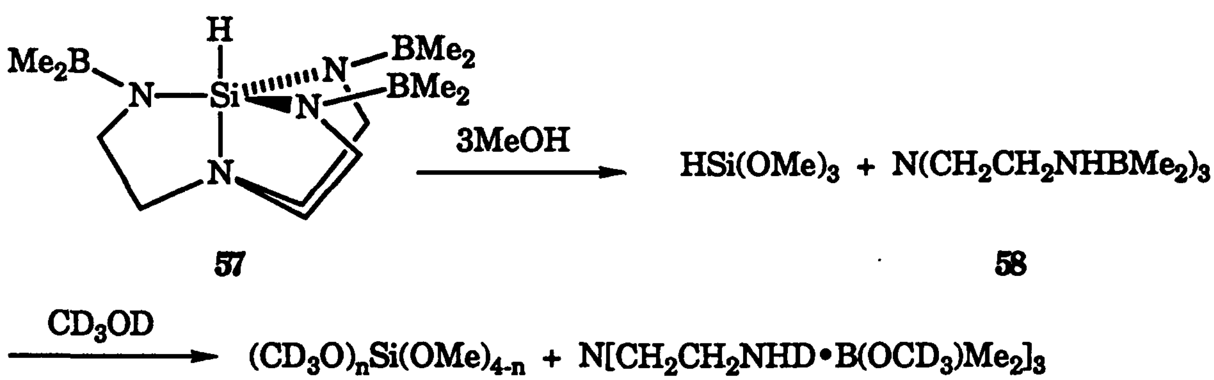

**Scheme IV**





55 56

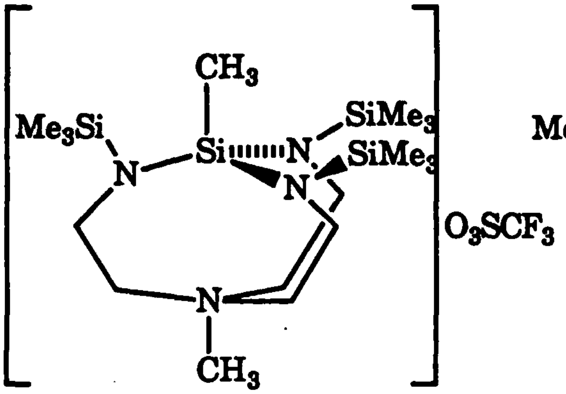
**Scheme V**

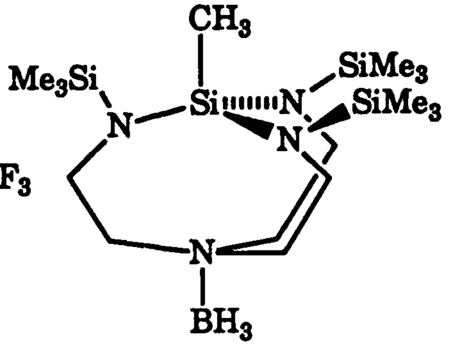


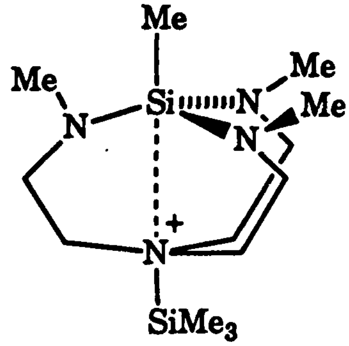
57 58 59

place by solvolytic cleavage of one of the Si-$N_{eq}$ bonds (e.g., **54**). The weakened Si-$N_{ax}$ interaction in **51** allowed us to synthesize **60**[14] in which the Si-$N_{ax}$ distance (3.561 Å)[15] has increased from 2.775 Å in **51** to being close to the van der Waals radius (3.65 Å). The $BH_3$ adduct of **51** (**61**) is currently being structured.[16]

The reaction in which equatorially silylated **38** is formed also affords the axially silylated isomer **62** in an equilibrium which depends upon solvent polarity and temperature.[12] Arguments substantiating the possibility of a hypercoordinate nitrogen in **62** have been brought forward.[13]



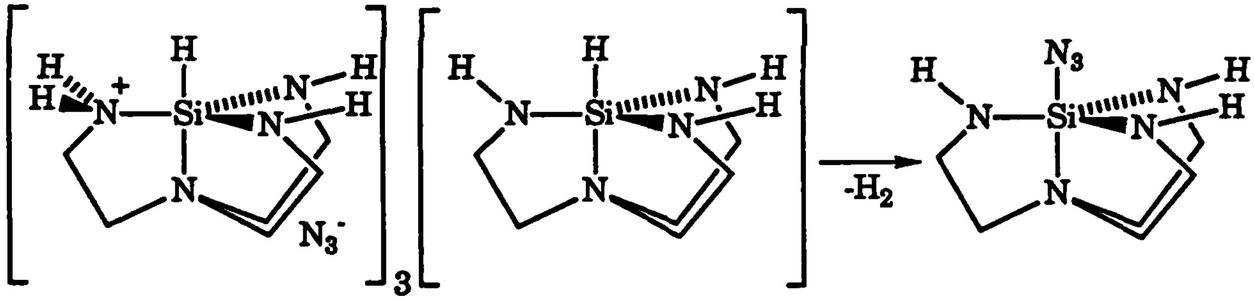




60 61 62

**B. Synthesis of silatranes pentacoordinated by nitrogen ligands**

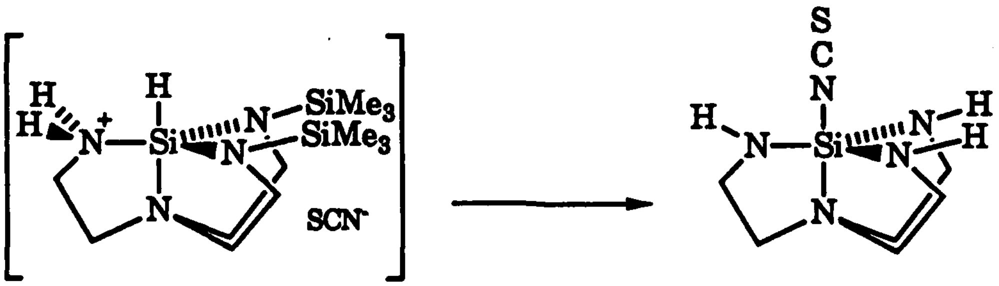
Although rational efforts to synthesize compounds of this type have thus far not been successful (See Section II. A. 1.; note however, **27**) compound **29** upon heating under vacuum yields **63**.[12] A similar reaction (also involving disproportionation, however)




(10)

29 63

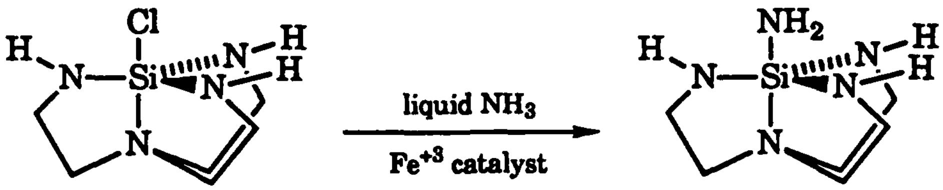
produces **64** from **33**.[12] These are the first reported examples of silatrane-type systems




(11)

33 64

containing five nitrogens coordinated to the silicon. We also have preliminary evidence that **65** is formed in reaction 12.[8]



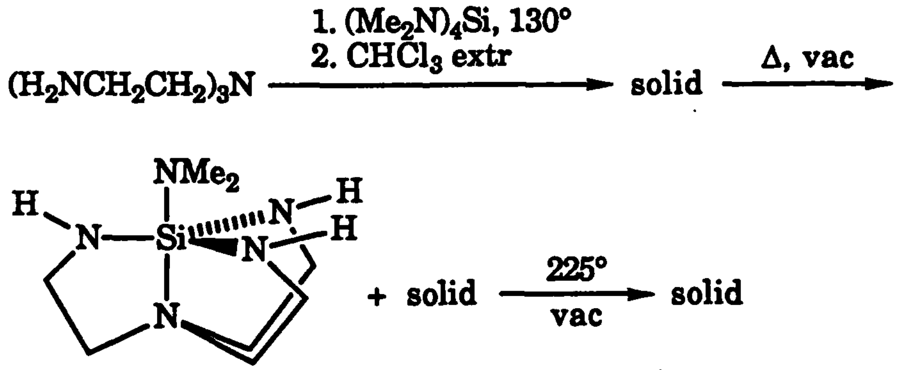

(12)

**20** **65**

### C. Synthesis of oligomers/polymers containing azasilatrane units

Two azasilatrane-based oligomers/polymers were partially characterized. The second step in Scheme VI gives rise to a small amount of a sublimate which may be **66**. Further heating of the residue gives a solid **67** which has appreciable solubility only in DMSO.

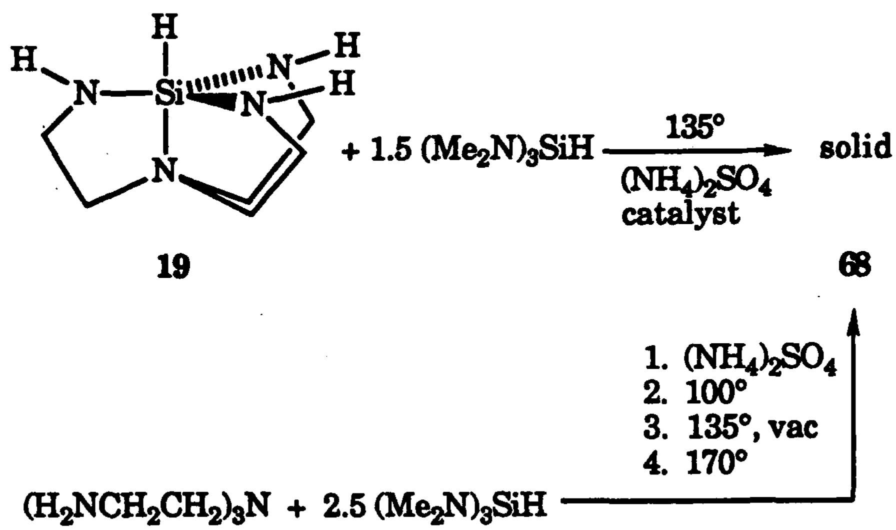
**Scheme VI**




**66** **67**

The alternate routes in Scheme VII give a solid **68** which, encouragingly, is chloroform soluble. The $^{29}Si$ NMR spectrum of **68** displays two broad peaks indicative of four-coordinate (-25 ppm) and five-coordinate (-77 ppm) silicon. The $^{1}H$ NMR spectrum exhibits $N(CH_3)_2$ peaks but no detectable N*H* resonance, suggesting that all three $N_{eq}$-H

**Scheme VII**




protons in **19** react with $(Me_2N)_3SiH$ possibly giving rise to "star" polymer in which the equatorial nitrogens in the triangular $SiN_3$ moieties of the azasilatrane units are bridged by $HSiNMe_2$ groups.

Polymers **69-71** shown in reactions 13-15, respectively, formed under similar

$$\mathbf{19} + 2.5\,HSi(NMe_2)_3 \xrightarrow[(NH_4)_2SO_4]{\Delta} \mathbf{69} \qquad (13)$$

$$\mathbf{19} + 0.35\,HSiCl_3 + HSi(NMe_2)_3 \xrightarrow[(NH_4)_2SO_4]{\Delta,\ Et_3N} \mathbf{70} \qquad (14)$$

$$\mathbf{47} + 2.25\,HSi(NMe_2)_3 \xrightarrow[(NH_4)_2SO_4]{\Delta} \mathbf{71} \qquad (15)$$

conditions and were studied by NMR spectroscopy in both solution and the solid state. $^{29}Si$ NMR studies confirm the presence of both four and five-coordinate Si in all cases. The absence of $NMe_2$ and NH functions in **69** was inferred from DEPT-$^{13}C$ and DEPT-$^{1}H$ spectra, respectively. While NH groups are not apparent in **70**, $NMe_2$ groups do appear in both the $^{1}H$ and $^{13}C$ NMR spectra. Using $^{1}H$ - $^{29}Si$ polarization transfer techniques, all the H-Si groups in **71** appear in the four-coordinate $^{29}Si$ region, while the MeSi moieties (originating from the starting atrane **47**) resonate in the five-coordinate $^{29}Si$ region. In

contrast to **69** and **70**, **71** possesses NH groups as judged from the $^1H$ NMR and IR spectra. The spectroscopic data are consistent with a linear polymer wherein one of the three NH functions on the silatrane **47** does not react.

**D. References** (Asterisked references represent publications supported by the AFOSR grant.)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